CATIONIC RHODIUM CYCLOOCTADIENE COMPLEXES WITH NITRILE LIGANDS

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(Received April 9th, 1979)

Summary

The synthesis and properties of complexes of the general formula $[Rh(COD)L_2]ClO_4$ (COD = 1,5-cyclooctadiene; L = monodentate nitrile group or L—L = bidentate nitrile group) and of mixed complexes of the type $[Rh(COD)LP(p\text{-}RC_6H_4)_3]A$ (P = triorganophosphine; A = ClO_4^- or BPh_4^-; R = F, H, CH_3, OCH_3) are described. These complexes react with molecular hydrogen to form species which catalyze the hydrogenation of terminal and cyclic olefins.

Introduction

Owing to their catalytic properties organorhodium(I) complexes containing tertiary phosphine groups have been extensively studied, but little work has been carried out on similar compounds containing nitrogen donor ligands.

Green et al. [1] have reported that the complex $[Rh(COD)(CH_3CN)_2]BF_4$ catalyses the hydrogenation of 1-hexene without concurrent isomerisation, and also the selective hydrogenation of 1,5-cyclooctadiene to cyclooctene. Recently, it was reported that cationic species of the type $[Rh(diolefin)L_2]^+$ (L = nitrogen donor ligand) catalyse the hydrogenation of olefins [2—5] and ketones [2,3] and the hydroformylation of olefins [5,6].

Mixed cationic complexes of the type $[Rh(COD)(py)PPh_3]PF_6$ [7] and $[Rh(NBD)(quin)PPh_3]ClO_4$ [4] (NBD = 2,5-norbornadiene, quin = quinoline) also catalize the hydrogenation of olefins.

In the present paper we describe the synthesis and catalytic behaviour of cationic rhodium(I) complexes containing nitrile ligands; these complexes have the general formulae $[Rh(COD)L_2]ClO_4$ and $[Rh(COD)LP(p\text{-}RC_6H_4)_3]ClO_4$ (R = F, H, CH_3, OCH_3).

Results and discussion

### Preparation and properties of complexes of the [Rh(COD)L₂]ClO₄ type

Preparation and properties of complexes of the [Rh(COD)L$_2$]ClO$_4$ type

[Rh(COD)$_2$]ClO$_4$ [8], prepared by the reaction of [Rh(COD)Cl]$_2$ with AgClO$_4$ in the presence of 1,5-cyclooctadiene, was treated in dichloromethane either with a slight excess of the bidentate dinitrile or with a large excess of the monodentate nitrile, according to eq. 1.

$$[Rh(COD)_2]ClO_4 + 2\ L\ (or\ L{-}L) \rightarrow [Rh(COD)L_2]ClO_4 + (COD) \tag{1}$$
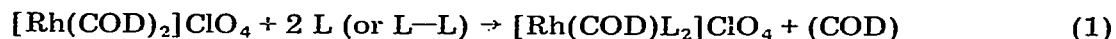
(The excess of the monodentate ligand is necessary to prevent reprecipitation of [Rh(COD)$_2$]ClO$_4$ upon the addition of ether). The ligands used were: acetonitrile (acn), benzonitrile (benzn), benzylnitrile (benln), *o*-tolunitrile (*o*-tolun), propionitrile (propn), butyronitrile (butn), malononitrile (maln), succinonitrile (sucn) and phthalonitrile (phthaln).

An alternative route involves the reaction of [Rh(COD)Cl]$_2$ with AgClO$_4$ in the presence of the appropriate nitrile, according to eq. 2.

$$\tfrac{1}{2}[Rh(COD)Cl]_2 + AgClO_4 + 2\ L\ (or\ L{-}L) \rightarrow [Rh(COD)L_2]ClO_4 + AgCl \tag{2}$$
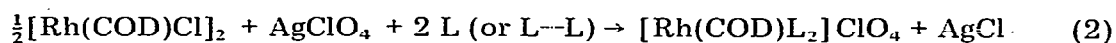
The product show a marked tendency to form oils, and completely anhydrous solvents must be used. The complexes were isolated as yellow microcrystalline solids (see Table 1), except for those with L = propionitrile or butyronitrile, which could only be obtained as yellow oils. Their characterization is based on their analogy with the other complexes, their IR spectra, and their reactions.

The nitrile groups can be readily displaced by other nitrogen donor groups, such as bipyridine or phenanthroline, to give complexes which have been reported previously [9].

On trying to isolate the cationic species [Rh(COD)L$_2$]$^+$ with BPh$_4^-$ as anion, in every case we obtained the complex Rh(COD)PhBPh$_3$ [10], in which the

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES [Rh(COD)L$_2$]ClO$_4$

| Complex	Found (calcd.)(%)			Λ_M (ohm^{-1} cm^2 mol^{-1})
	C	H	N	
[Rh(COD)(acn)$_2$]ClO$_4$ (I)	37.15 (36.71)	4.93 (4.62)	7.01 (7.13)	128
[Rh(COD)(benzn)$_2$]ClO$_4$ (II)	51.65 (51.13)	3.99 (4.29)	5.33 (5.42)	110
[Rh(COD)(benln)$_2$]ClO$_4$ (III)	52.95 (52.90)	5.08 (4.81)	5.24 (5.14)	136
[Rh(COD)(*o*-tolun)$_2$]ClO$_4$ (IV)	53.04 (52.90)	4.87 (4.81)	4.55 (5.14)	113
[Rh(COD)(maln)]ClO$_4$ (VII)	36.10 (35.08)	3.89 (3.75)	7.55 (7.44)	119
[Rh(COD)(sucn)]ClO$_4$ (VIII)	35.82 (36.89)	4.08 (4.13)	6.86 (7.17)	111
[Rh(COD)(phthaln)]ClO$_4$ (IX)	42.80 (43.80)	3.74 (3.68)	5.80 (6.38)	135

tetraphenylborate is coordinated via an arene ring (eq. 3)

$$[Rh(COD)L_2]^+ + BPh_4^- \rightarrow Rh(COD)PhBPh_3 + 2\ L\ (or\ L{-}L) \qquad (3)$$

Complexes of the [Rh(CO)$_2$L$_2$]ClO$_4$ type

Bubbling of carbon monoxide at atmospheric pressure through an acetone solution of the [Rh(COD)L$_2$]ClO$_4$ complexes for a few minutes gave carbonyls, which were not isolated as solids *. Their IR spectra show two strong bands due to ν(CO) assignable to a *cis*-dicarbonyl [13] formed according to eq. 4.

$$[Rh(COD)L_2]ClO_4 + 2\ CO \rightarrow cis\text{-}[Rh(CO)_2L_2]ClO_4 + (COD) \qquad (4)$$

The assignment of the structure was based on the following observations.

(i) Treatment of [Rh(CO)$_2$Cl]$_2$ with AgClO$_4$ in acetone gives the non-isolable solvated complex [Rh(CO)$_2$(acetone)$_x$]ClO$_4$ [11], solutions of which react with nitrile according to eq. 5 to give the corresponding dicarbonyl derivatives.

$$[Rh(CO)_2(acetone)_x]ClO_4 + 2\ L\ (or\ L{-}L) \rightarrow [Rh(CO)_2L_2]ClO_4 + x\ acetone \quad (5)$$
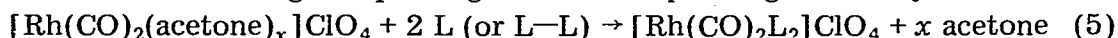
Their IR spectra are identical to those of the products obtained by the direct carbonylation of [Rh(COD)L$_2$]ClO$_4$ (see eq. 4).

(ii) Addition of bipy to the complexes formed in process (4) gives the previously described [9] *cis*-dicarbonyl derivative [Rh(CO)$_2$(bipy)]ClO$_4$.

Complexes of the [Rh(COD)LP(p-RC$_6$H$_4$)$_3$]A type (A = ClO$_4^-$ or BPh$_4^-$)

Addition of two mol of PPh$_3$ to the nitrile complexes leads to [Rh(COD)(PPh$_3$)$_2$]ClO$_4$, while addition of one mol of PPh$_3$, to complexes containing monodentate nitrile ligands gives the corresponding mixed complexes (eq. 6).

$$[Rh(COD)_2]ClO_4 \xrightarrow[-COD]{+2L} [Rh(COD)L_2]ClO_4 \xrightarrow[-L]{+PPh_3} [Rh(COD)LPPh_3]ClO_4 \qquad (6)$$
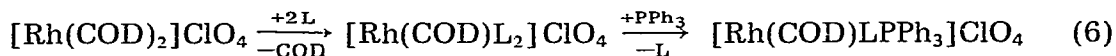
We were able to isolate such complexes having L = acetonitrile (X), benzylnitrile (XI), acrylonitrile [Rh(COD)(acryn)PPh$_3$]ClO$_4$ (XII), as well as derivatives of the general formula [Rh(COD)(acn)P(p-RC$_6$H$_4$)$_3$]ClO$_4$ (see Table 2).

As shown in eq. 3, addition of BPh$_4^-$ to [Rh(COD)L$_2$]$^+$ leads to the neutral complex Rh(COD)PhBPh$_3$, but the complexes [Rh(COD)LPPh$_3$]$^+$ can be obtained by adding PPh$_3$ before the BPh$_4^-$. Thus we were able to obtain the acetonitrile complex [Rh(COD)(acn)PPh$_3$]BPh$_4$ (XVI) and the corresponding propionitrile (XVII) and butyronitrile (XVIII) compounds. The bis-nitrile derivatives [Rh(COD)L$_2$]ClO$_4$ (L = propn, butn) could not be isolated as solids because of their tendency to form oils.

The analytical data for the novel mixed compounds are listed in Table 2.

IR spectra

The cationic complexes show bands due to the perchlorate anion ClO$_4^-$ (T_d) [14] at ca. 1100 and 620 cm^{-1}, whereas the corresponding tetraphenylborate derivatives exhibit two strong bands at ca. 1480 and 1425 cm^{-1}, which are

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* The syntheses of [Rh(CO)$_2$(acn)$_2$]A from [Rh(CO)$_2$Cl]$_2$ [11] or [Rh(acn)$_4$(NO)]A [12] have been previously reported.

TABLE 2

ANALYTICAL DATA FOR THE COMPLEXES [Rh(COD)LP(p-RC$_6$H$_4$)$_3$]ClO$_4$

Complex	Found (calcd.)(%)			Λ_M (ohm^{-1} cm^2 mol^{-1})
	C	H	N	
[Rh(COD)(acn)PPh$_3$]ClO$_4$ (X)	53.31 (54.76)	4.86 (4.93)	2.13 (2.28)	121
[Rh(COD)(benln)PPh$_3$]ClO$_4$ (XI)	58.62 (59.16)	5.14 (4.97)	2.17 (2.03)	121
[Rh(COD)(acryn)PPh$_3$]ClO$_4$ (XII)	56.37 (55.63)	4.83 (4.83)	2.20 (2.24)	119
[Rh(COD)(acn)P(p-CH$_3$OC$_6$H$_4$)$_3$]ClO$_4$ (XIII)	52.72 (52.87)	4.71 (5.16)	1.93 (1.99)	116
[Rh(COD)(acn)P(p-CH$_3$C$_6$H$_4$)$_3$]ClO$_4$ (XIV)	56.04 (56.74)	5.44 (5.53)	2.07 (2.14)	120
[Rh(COD)(acn)P(p-FC$_6$H$_4$)$_3$]ClO$_4$ (XV)	50.64 (50.19)	3.60 (4.06)	2.13 (2.09)	116
[Rh(COD)(acn)PPh$_3$]BPh$_4$ (XVI)	75.25 (74.90)	6.02 (6.05)	1.56 (1.68)	27
[Rh(COD)(propn)PPh$_3$]BPh$_4$ (XVII)	74.78 (75.01)	5.99 (6.18)	1.62 (1.65)	25
[Rh(COD)(butn)PPh$_3$]BPh$_4$ (XVIII)	75.51 (75.25)	6.36 (6.32)	1.38 (1.63)	26

assignable to an in-plane skeletal C—C stretching of the phenyl rings of the uncomplexed tetraphenylborate ion [10].

The cationic complexes [Rh(COD)L$_2$]ClO$_4$ and [Rh(COD)LP(p-RC$_6$H$_4$)$_3$]A show absorptions characteristic of the coordinated cyclooctadiene, along with bands due to the various ligands. Table 3 lists the vibrations due to ν(CN) of the coordinated or free nitrile groups together with $\Delta\nu$(CN) = ν(CN)(complex) — ν(CN)(free ligand).

TABLE 3

IR SPECTRA OF THE COMPLEXES PREPARED

Complex	ν(CN) [a]		$\Delta\nu$(CN) [b]
	Complex	Free ligand	
[Rh(COD)(acn)$_2$]ClO$_4$ (I)	2290	2254 [d]	36
[Rh(COD)(benzn)$_2$]ClO$_4$ (II)	2260	2231 [d]	29
[Rh(COD)(benln)$_2$]ClO$_4$ (III)	2275	2255 [e]	20
[Rh(COD)(o-tolun)$_2$]ClO$_4$ (IV)	2250	2222 [e]	28
[Rh(COD)(propn)$_2$]ClO$_4$ (V)	2285	2248 [d]	37
[Rh(COD)(butn)$_2$]ClO$_4$ (VI)	2283	2250 [e]	33
[Rh(COD)(maln)]ClO$_4$ (VII)	2315	2278 [c]	37
[Rh(COD)(sucn)]ClO$_4$ (VIII)	2300	2257 [c]	43
[Rh(COD)(phthaln)]ClO$_4$ (IX)	2264	2230 [c]	34
[Rh(COD)(acn)PPh$_3$]ClO$_4$ (X)	2300	2254 [d]	46
[Rh(COD)(benln)PPh$_3$]ClO$_4$ (XI)	2295	2255 [e]	40
[Rh(COD)(acryn)PPh$_3$]ClO$_4$ (XII)	2255	2228 [d]	27
[Rh(COD)(propn)PPh$_3$]BPh$_4$ (XVII)	2275	2248 [d]	27
[Rh(COD)(butn)PPh$_3$]BPh$_4$ (XVIII)	2273	2250 [e]	23

[a] Nujol mulls for the perchlorate complexes, KBr disks for the tetraphenylborate complexes. [b] Change in ν(CN) on coordination. [c] Ref. 22. [d] Ref. 17. [e] CHCl$_3$ solution.

The increase in the nitrile stretching frequency upon coordination to the rhodium atom ($\Delta\nu$(CN) 20—50 cm^{-1}), which is observed in every case, indicates coordination of the organonitrile ligands to the rhodium atom via σ donation of the lone pair of electrons on the nitrile nitrogen atom [15—17]. The aceto-nitrile complexes show two absorptions in the nitrile region; those in the 2300—2290 cm^{-1} range are assignable to ν(CN), whilst those at 2330—2310 cm^{-1} are assigned to combination bands δ(CH$_3$) + ν(CC) [18—20].

The IR spectrum of XII shows bands due to ν(C=C) which are assignable to the uncoordinated C=C bond of the acrylonitrile ligand, whereas the value of $\Delta\nu$(CN) (see Table 3) indicates that the ligand acts as monodentate, coordinated through the nitrogen lone-pair.

The carbonyl complexes [Rh(CO)$_2$L$_2$]ClO$_4$ show two strong bands at ca. 2060 and 1985 cm^{-1}, which point to a cis-dicarbonyl configuration [13].

Conductivities

The conductivities, measured with 5×10^{-4} M acetone solutions, show that the complexes [Rh(COD)L$_2$]ClO$_4$ and [Rh(COD)LP(p-RC$_6$H$_4$)$_3$]ClO$_4$ (Λ_M 110—150 ohm^{-1} cm^2 mol^{-1}) are 1/1 electrolytes.

The complexes [Rh(COD)LP(p-RC$_6$H$_4$)$_3$]BPh$_4$ give Λ_M values of 25—30 ohm^{-1} cm^2 mol^{-1}, which are much too low for the bulky anion BPh$_4^-$ [21], and suggest the existence of an equilibrium in solution:

[Rh(COD)LP(p-RC$_6$H$_4$)$_3$]BPh$_4$ $\leftrightharpoons$ Rh(COD)PhBPh$_3$ + L + P(p-RC$_6$H$_4$)$_3$

In the solid state these complexes, however, contain the uncoordinated anion BPh$_4^-$, as is clearly shown by their IR spectra.

Behaviour as catalysts

Acetone solutions of the cationic diolefin complexes react with molecular hydrogen at atmospheric pressure and room temperature to give species which catalyze the hydrogenation of cyclic and terminal olefins. Table 4 shows the

TABLE 4

CATALYSTS, CONDITIONS AND RATES IN THE HYDROGENATION OF 1-HEXENE AND CYCLO-HEXENE

Catalyst	Rate of reduction (mol(mol Rh)$^{-1}$ (min)$^{-1}$ of hydrogen uptake) [a]	
	1-Hexene	Cyclohexene
[Rh(COD)(acn)$_2$]ClO$_4$	2.6	4.9
[Rh(COD)(acn)P(p-CH$_3$OC$_6$H$_4$)$_3$]ClO$_4$	6.6	7.0
[Rh(COD)(acn)P(p-CH$_3$C$_6$H$_4$)$_3$]ClO$_4$	2.7	2.2
[Rh(COD)(acn)PPh$_3$]ClO$_4$	2.0	2.2
[Rh(COD)(acn)P(p-FC$_6$H$_4$)$_3$]ClO$_4$	1.4	1.8
[Rh(COD)(benzn)$_2$]ClO$_4$	1.4	1.1
[Rh(COD)(sucn)]ClO$_4$	3.8	2.7
[Rh(COD)(maln)]ClO$_4$	<0.1	<0.1
[Rh(COD)(phthaln)]ClO$_4$	<0.1	<0.1

[a] Substrate, 2×10^{-1} M; catalyst 2×10^{-3} M; temperature, 25°C; volume of solution, 15 cm^3 (acetone).

TABLE 5

THE HYDROGENATION OF SOME UNSATURATED SUBSTRATES WITH [Rh(COD)(acn)$_2$]ClO$_4$

Substrate	Rate of disappearance a mol (mol Rh)$^{-1}$ (min)$^{-1}$	Products after t minutes			
		Substrate	Alkene	Alkane	t
2,3-Dimethyl-1,3-butadiene	1.6	0	69	31	85
2-Methyl-1,3-butadiene	0.4	0	68	32	230
1,4-Cyclohexadiene	6.7	4	32	64	21
1-Hexyne	0.3	54	13	34	200

a Substrate, 2 X 10^{-1} M; catalyst, 2 X 10^{-3} M; temperature, 25°C; volume of solution, 15 cm^3 (acetone was used as solvent except for 2,3-dimethyl-1,3-butadiene(acetone/dichloromethane, 1 : 1)).

reduction rates of 1-hexene and cyclohexene for some representative complexes. The formation of the catalytically active species requires a prehydrogenation period, though prolongation of this prehydrogenation may lead to some decomposition of the catalyst.

It is noteworthy that the reduction in the presence of [Rh(COD)(acn)$_2$] ClO$_4$ is faster for cyclohexene than for 1-hexene. Nonetheless, the catalytic hydrogenation of equimolecular mixtures of hexene and cyclohexene shows that the former is preferentially hydrogenated, in accordance with its higher coordination capacity.

Experiments with mixed complexes of the type [Rh(COD)(acn)-P(p-RC$_6$H$_4$)$_3$]ClO$_4$ (R = F, H, CH$_3$ or OCH$_3$) reveal that the reduction rate for the different olefins increases with increasing basicity of the relevant phosphine (F < H < CH$_3$ < OCH$_3$), as previously observed for the neutral complexes RhCl-[P(p-RC$_6$H$_4$)$_3$]$_3$ [23,24].

As may be seen in Table 5, the hydrogenation of diolefins and 1-hexyne catalyzed by [Rh(COD)(acn)$_2$]ClO$_4$ reveals the relatively poor selectivity of this catalyst in contrast with that reported by Schrock and Osborn for cationic complexes containing tertiary phosphine groups [25].

Experimental

The C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer. Conductivities were measured in ca. 5 X 10^{-4} M acetone solution with a Philips 9501/01 conductimeter. The IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol mulls between polyethylene sheets or potassium bromide discs.

The catalytic activity was examined in a conventional hydrogenation apparatus, provided with a septum. The introduction of the reactants into the reaction flask was always carried out in the following order: solution of the catalyst, hydrogen (initial pressure 1 atm), substrate. A substrate/catalyst ratio of 100/1 was used in 15 cm^3 of solution. (Slight decomposition of the catalyst was sometimes observed). The hydrogenation rate was determined by analyzing the products in a Perkin—Elmer 3920B chromatograph. The peak areas were determined with a Minigrator Computing Integrator.

The rates listed in Tables 4 and 5 are the highest observed; in some cases, the

reproducibility was poor, because of decomposition, which may vary from one run to the next.

All the solvents were dried and distilled before the preparations and the catalytic experiments.

Synthesis of complexes of the [Rh(COD)L₂]ClO₄ type (I—IV; VII—IX)

The addition of the corresponding nitrile ligand to a dichloromethane solution of [Rh(COD)₂]ClO₄ caused an instantaneous change of colour. The resulting complexes were precipitated by addition of ether and separated by filtration.

The monodentate nitrile ligands were added in a 10/1 ratio, whilst a 1.2/1 ratio was used for bidentate nitrile ligands.

Carbonylation reactions

Carbon monoxide (1 atm) was bubbled for 25 min through dichloromethane solutions of the appropriate complex.

Synthesis of complexes of the [Rh(COD)LP(p-RC₆H₄)₃]ClO₄ type (X—XV)

Addition of an equimolar amount of triarylphosphine to the yellow solution obtained by reacting [Rh(COD)₂]ClO₄ with an excess of the nitrile gave the corresponding mixed complex, which was precipitated by addition of ether.

Synthesis of complexes of the [Rh(COD)LPPh₃]BPh₄ type (XVI—XVIII)

Nitrile was added to a methanol suspension of [Rh(COD)Cl]₂ until complete solubilization, whereupon stoichiometric amounts of PPh₃ were added. The precipitation of the required complexes was accomplished by addition of NaBPh₄. They were isolated by filtration and washed with methanol/water, methanol and finally ether.

Acknowledgements

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